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LEAD ARSENATE AND PARIS GREEN.

- I. Their Chemical Composition. By John Phillips Street, M.S.
II. Directions for their Use as Insecticides.
By W. E. Britton, Ph.D.
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LEAD ARSENATE AND PARIS GREEN.

I. THEIR CHEMICAL COMPOSITION.

BY JOHN PHILLIPS STREET.*

The constantly increasing use of insecticides in various spraying mixtures makes the effectiveness and the cheapness of the poisons used a matter of considerable practical importance. Paris green has been more commonly used for many years than any other arsenical insecticide, and has proved very effective. There is, however, a certain serious objection to its use; the partial solubility in water of the arsenious oxid, which frequently causes damage to foliage. For this reason entomologists have sought a different poison, which would be effective against insects, harmless to plants, and economical for the farmer to use. Lead arsenate seems to meet these requirements, and possesses a still further advantage over Paris green in that its mechanical condition keeps it longer in suspension in the spraying mixture. There are a number of brands of this material on the market, varying greatly in appearance and consistency, and it was considered advisable to make a somewhat extended chemical examination of them to determine their relative value. As the various brands of Paris green on sale in this State had never been analysed at this Station, they also have been included in this examination.

METHODS OF ANALYSIS.

In the analysis of lead arsenate the method proposed by Haywood† has been followed in all particulars, and has proved very satisfactory. With Paris green the same methods as used by the writer‡ in a similar examination at the New Jersey Station have

* The analyses of Paris green have been made by Messrs. E. M. Bailey and E. J. Shanley; those of lead arsenate by the writer.

† U. S. Dept. of Agl., Bur. of Chem., Bull. 105, 165.

‡ New Jersey Expt. Station, Bull. 195.

been followed. In addition, however, a test of the water-solubility of the arsenious oxid was made by the official A. O. A. C. method,* treating the green with distilled water for ten days.

LEAD ARSENATE.

Ten of the eleven samples analysed were taken from the museum stock of Dr. Britton, the State entomologist, but were recently acquired and were believed to be representative; the duplicate sample of Swift's arsenate was bought in the open market. The samples were received in containers of various sizes and material, from a one-pound glass jar to a fourteen pound wooden bucket. The material itself showed striking differences in consistency. Disparene settled out completely, leaving a supernatant liquid filling from one-fourth to one-third of the vessel; the Target brand and Swift's also showed some separated liquid, while the others were more of the consistency of putty and quite homogeneous.

The samples analysed were as follows:

19210. Eagle Brand. Adler Color & Chemical Co., New York.

19212. Target Brand. American Horticultural Distributing Co., Martinsburg, W. Va.

19211. Disparene. The Bowker Co., Boston, Mass.

19216. Star Brand. Fred. L. Lavanburg, New York.

19215. Anchor Brand. Leggett & Bro., New York.

19213. Swift's Arsenate. Merrimac Chemical Co., Boston, Mass.

18703. Duplicate of No. **19213**, purchased in market.

19643. Arsenate of Lead. Monmouth Chemical Works, Shrewsbury, N. J.

19357. Arsenate of Lead. The Powers-Weightman-Rosengarten Co., Philadelphia, Pa.

19358. Aiboneta. Schoonmaker & Son, Cedar Hill-on-Hudson, N. Y.

19209. Arsenate of Lead. The Vreeland Chemical Co., New York.

* U. S. Dept. of Agl., Bur. of Chem., Circ. 10, 3.

ANALYSES OF ARSENATE OF LEAD.

Station No.	Brand.	Original Material.						Water-Free.		
		Water.	Arsenic Oxide (As ₂ O ₃).	Lead Oxide (PbO).	Soluble Impurities (other than As ₂ O ₃ and PbO).	Insoluble Impurities (by difference).	Soluble Arsenic Oxide.	Arsenic Oxide (As ₂ O ₃).	Lead Oxide (PbO).	Total Impurities.
19210	Eagle	54.55	14.89	28.46	0.32	1.78	0.46	32.76	62.62	4.62
19212	Target	50.30	12.30	34.03	2.73	0.64	1.31	24.75	68.47	6.78
19211	Disparene	46.47	13.87	35.11	4.34	0.21	0.39	25.91	65.59	8.50
19216	Star	50.57	12.64	35.63	0.47	0.69	0.51	25.57	72.08	2.35
19215	Anchor	35.59	17.11	44.05	2.02	1.23	0.86	26.56	68.39	5.05
19215	Swift's	49.95	14.91	33.08	0.80	1.26	0.57	29.79	66.09	4.12
18703	"	48.40	15.19	33.78	0.88	1.75	0.30	29.44	65.47	5.09
19643	Monmouth	58.44	11.29	25.59	1.41	3.27	0.50	27.17	61.57	11.26
19357	Powers-Weightman	51.79	11.42	33.70	2.69	0.40	0.22	23.69	69.90	6.41
19358	Aiboneta	41.95	11.72	37.90	7.94	0.49	0.42	20.19	65.29	14.52
19209	Vreeland	33.65	21.91	41.44	0.74	2.26	0.86	33.02	62.46	4.52

RESULTS OF ANALYSES.

The analyses show lead arsenate to be far from a uniform material; the arsenic oxide ranges from 11.29 to 21.91 per cent., and the lead oxide from 25.59 to 44.05 per cent. The soluble arsenic oxide was low in all cases, ranging from 0.22 to 1.31 per cent., and this after a treatment for ten days. No soluble lead oxide was found in any of the samples. The nature of the impurities was not determined in any case; **19210**, **19358**, **19643** and **19357**, however, showed traces of nitrates. The impurities were not high except in three samples, **19211**, **19643** and **19358**; neither Disparene nor Aiboneta was sold as pure lead arsenate and therefore cannot be considered adulterated; the Monmouth sample, however, was sold as a pure material; in addition to its high content of impurities, it also contains the lowest percentages of both arsenic and lead oxids.

Lead arsenate is usually prepared by the action of lead acetate on disodium arsenate; some manufacturers, however, substitute lead nitrate for the acetate. Smith* has shown that the commercial grades of sodium arsenate and lead acetate and nitrate vary considerably. He found the lead oxide in lead acetate varied from 58.81 to 66.80 per cent., and in lead nitrate from 66.37 to

* Agr. Massachusetts, 1897, 357-369.

68.37 per cent.; while in sodium arsenate the arsenic oxid varied from 36.77 to 47.80 per cent. The calculation of the theoretical composition of commercial lead arsenate is, therefore, attended with some difficulty. Haywood,* however, has shown that, with pure chemicals, where lead acetate is used the theoretical composition should be 74.40 per cent. lead oxide and 25.60 per cent. arsenic oxide; and where lead nitrate is used, 64.26 and 33.15 per cent., respectively. The methods used in the above analyses give results very close to theory where the lead arsenate is prepared from lead nitrate, but where lead acetate is used slightly higher than theory for arsenic oxide and slightly lower for lead oxide, indicating that probably some secondary reaction takes place during the process of manufacture, resulting in the formation of some compound other than lead arsenate, probably an acid lead arsenate. By referring to the analyses of the samples on the water-free basis, it appears that **18703, 19209, 19210, 19213** and **19643** are made from lead nitrate, the others from lead acetate. Formerly it was the practice to add glucose to increase the adhesive power of the arsenate, but it has been shown that it adheres almost as well without glucose as with it, and its use has been largely discontinued.

Allowing for the variations in process of manufacture, it would seem, however, that the content of arsenic oxid in the various commercial lead arsenates was conditioned more by the wetness of the material than anything else; the content of water in the samples analysed ranged from 33.65 to 58.44 per cent. A perfectly dry material has not been found advantageous, for while even in such a form it remains in suspension several times as long as the finest Paris green, it settles about three times as fast as when the arsenate is used in the form of a paste. On the other hand, the paste must not be too tenacious or it will be difficult to break up and distribute evenly throughout the spraying mixture. Colby† has found this objection to hold with Disparene. In making the water-soluble determinations it was observed that there were marked variations in the rate of settling even when the samples were in the dry and powdered condition. It is probable that the same peculiarity would have been noted in the samples in their original state, but as in most cases the

* U. S. Dept. of Agl., Bur. of Chem., Bull. 105, 163.

† California Expt. Station, Bull. 151.

whole sample had already been dried, verification of this supposition was impossible.

HOME-MADE LEAD ARSENATE.

It has frequently been recommended that farmers prepare their own lead arsenate as they need it. Colby* recommends the following formula: Dissolve 24 oz. of lead acetate or 20 oz. of lead nitrate in one gallon of cold water; also separately dissolve 10 oz. sodium arsenate in three quarts of water, both solutions to be made in wooden vessels. Pour the separate solutions into the spray tank containing from 100 to 150 gallons of water; a white precipitate of lead arsenate immediately forms. This preparation may be made several times stronger without the least danger of injury to the foliage. The freshly precipitated home-made arsenate seems to keep in suspension better than even the best commercial preparations.

COST OF LEAD ARSENATE.

As stated before, only one of the samples was bought in the open market; the prices have therefore not been affixed in any case. By correspondence with the manufacturers the Station received quotations as follows: In 100 lb. kegs, from 9.5 to 13 cents per lb.; in 5 to 20 lb. buckets, from 11 to 16 cents per lb.; and in 1 lb. cans from 11.5 to 17 cents per lb. The advantage of purchasing in quantity is apparent.

ITS ADVANTAGES.

Lead arsenate is very effective against leaf-eating insects. Its chief advantages over Paris green are its greater adhesive power and its harmlessness to the foliage. A single treatment of lead arsenate will adhere to the foliage for a period during which two or three sprayings with Paris green would be necessary to secure the same effect. The insolubility of its arsenic makes possible the use of large quantities without danger even in inexperienced hands. From the standpoint of effectiveness lead arsenate, although containing but from one-third to one-fourth as much actual arsenic as Paris green, is nearly as economical as the latter poison when sold at the same price. Purchased at the wholesale quotations noted elsewhere, and considering the duration and safety of its action, it is actually somewhat cheaper than Paris

* Loc. cit.

green. Furthermore, its greater power of suspension makes it more easily used and insures a more uniform distribution of the poison over the plant.

PARIS GREEN.

There is no law in this State regulating the sale of Paris green, but where a state inspection is in effect the requirements are generally very similar to those in the New Jersey law,* section 3 of which reads:

"Paris green, or any product analogous to it, when sold, offered or exposed for sale as such, in this State, shall comply with the following requirements:

"First. It shall contain arsenic, in combination with copper, equivalent to not less than fifty per centum arsenious oxide.

"Second. It shall not contain arsenic in water-soluble forms equivalent to more than three and one-half per centum of arsenious oxide."

Many analyses of Paris green have been made by the various Experiment Stations, showing the green to be of variable composition. These variations are chiefly due to different methods of manufacture or carelessness in carrying out the same. In many cases a large amount of the arsenic exists as free arsenious oxid, which may arise from intentional addition of white arsenic, as well as from careless manufacture. This is a serious adulteration, for white arsenic is a cheaper material, and its solubility in water renders its presence in anything but small quantities a source of much danger to foliage from scorching. Other adulterations have been detected, but the one just referred to is the most prevalent and most objectionable.

Paris green is essentially copper aceto-arsenite, and, if pure, should contain an equivalent of 58.65 per cent. arsenious oxide, 31.29 copper oxide and 10.06 acetic acid. The commercial article, however, usually contains small quantities of moisture and sand and varying amounts of sodium sulphate.

Twelve samples, representing eight manufacturers, were purchased from dealers by the Station sampling agent. A description of these follows:

19481. Made by A. B. Ansbacher & Co., New York. Sold by Lyon & Ewald, New London.

18662. Made by A. B. Ansbacher & Co., New York. Sold by the Sisson Drug Co., Hartford.

* New Jersey Expt. Station, Bull. 195.

18634. Made by E. J. Barry, New York. Sold by Odell's Pharmacy, New Britain.

18509. Made by E. J. Barry, New York. Sold by J. H. & W. E. Cone, Hartford.

18704. Made by James A. Blanchard, New York. Sold by F. S. Platt, New Haven.

19547. Made by Morris Hermann & Co., New York. Sold by D. B. Wilson Co., Waterbury.

18569. Made by Leggett & Bro., New York. Sold by Lockwood & Palmer, Stamford.

18508. Made by Leggett & Bro., New York. Sold by M. H. Mallett, New Milford.

18512. Made by I. Pfeiffer, New York. Sold by Frank M. West, Bridgeport.

18510. Made by C. T. Reynolds & Co., New York. Sold by H. K. Brainard, Thompsonville.

18511. Made by C. T. Reynolds & Co., New York. Sold by Danbury Hardware Co., Danbury.

18663. Made by The Sherwin-Williams Co., Newark, N. J. Sold by R. E. Page, Hartford.

ANALYSES OF PARIS GREEN.

Station No.	Manufacturer.	Cost of Package.	Weight of Package.		Arsenious Oxide. (As ₂ O ₃).			Copper Oxide, (CuO).	Arsenious Oxide combined with copper.
			Claimed.	Found.	Total.	Water-Soluble, 1 day.	Water-Soluble, 10 days.		
		cts.	oz.	oz.	%	%	%	%	%
19481	Ansbacher	13	* 4	3.6	57.92	1.46	2.92	28.76	53.78
18662	“	10	4	4.0	57.44	0.97	2.44	29.49	55.15
18634	Barry	35	* 16	14.5	57.23	1.71	6.82	29.55	55.26
18509	“	18	* 8	8.0	56.62	2.44	6.82	29.01	54.25
18704	Blanchard	10	4	5.0	57.03	2.44	7.31	28.14	52.62
19547	Hermann	18	* 8	7.6	56.20	2.44	4.87	28.54	53.37
18569	Leggett	10	* 4	3.6	60.61	5.85	10.72	27.15	50.77
18508	“	20	8	7.3	56.83	2.92	8.77	29.34	54.87
18512	Pfeiffer	20	8	8.0	56.71	1.46	4.38	30.27	56.60
18510	Raynolds	28	* 16	15.4	60.83	1.95	6.32	26.56	49.63
18511	“	10	* 4	4.0	61.19	2.44	9.74	27.15	50.77
18663	Sherwin-Williams	10	4	3.6	56.56	1.46	2.92	29.88	55.88

* Weight printed on label ; in all other cases the weight is assumed from the size of package and price asked.

All the samples were carefully weighed with and without the container; one sample was overweight, four equalled the weight claimed, and seven were short weight. These shortages varied from 4 to 10 per cent., not large in any case, but indicating that the manufacturers' claimed weight is intended to include the weight of the container as well as the green itself, a practice without justification.

CHEMICAL ANALYSIS.

Total Arsenious Oxide. All the samples contained satisfactory amounts of total arsenious oxide, varying from 56.20 to 61.19 per cent. with an average of 57.93 per cent.; this average is only slightly lower than the equivalent of arsenious oxide contained in pure copper aceto-arsenite. Judging, therefore, alone from the content of arsenious oxide, it would appear that the Paris green on the market in Connecticut is of high quality. A definite decision as to the purity of the green, however, cannot be reached without considering also the amount of water-soluble arsenic present.

Water-Soluble Arsenious Oxide. Free arsenious oxide is always soluble in water, and the combined arsenic is liable to be rendered soluble by prolonged treatment. Two methods for determining soluble arsenious oxide have been adopted provisionally by the Association of Official Agricultural Chemists, in one of which sodium acetate is used as the solvent, while in the other the green is treated with water for ten days. Investigations with these methods have shown that the sodium acetate method gives more closely the true percentage of free arsenious oxide, while the water-extraction method gives in addition some arsenic caused by the decomposition of the green by water. From a practical standpoint the portion of the green that is so loosely combined would in all likelihood soon break up and scorch the foliage quite as badly as would free arsenious oxide. The water-extraction method would seem, therefore, to indicate more accurately the probable effect of the green on foliage.

The provisional method of the A. O. A. C. requires treatment with water for ten days, but it has been pointed out that the usual practice among horticulturists is to mix the green with water not very long before they wish to use it. For this reason certain Stations, for instance New York, California and New Jersey,

have adopted a one-day extraction period, which it is believed gives results more in harmony with actual practice. This Station has likewise adopted this method in the present work, and analyses by both the one-day and ten-day extractions are given in the table for comparison. The analyses clearly show that, if the ten-day method is to prevail as a standard, but three of the samples would fall within the usual legal limit of three and one-half to four per cent. of soluble arsenious oxide. With the one-day method, but one sample, **18569**, contains an excessive amount, 5.85 per cent. This sample varies greatly in composition from a duplicate sample from the same manufacturer, and under the microscope clearly shows the presence of white arsenic. The use of this sample would be exceedingly dangerous to foliage.

Copper Oxide. The amount of cupric oxide found in the samples varied from 26.56 to 30.27 per cent., with an average of 28.65 per cent. In pure copper aceto-arsenite the ratio of arsenious oxide to copper oxide is as 1.87 is to 1.00. This ratio is of value in assisting to determine whether white arsenic has been used to fortify the green, for arsenious oxide cannot be added without increasing the ratio. In the samples analysed, the ratio varied from 1.87 to 2.29; the high ratio shown in sample **18569** gives additional evidence of the presence of considerable quantities of white arsenic. The amount of arsenious oxide in combination with copper varied from 49.63 to 55.88 per cent., with one exception above the usual legal requirement of 50 per cent. In three of the samples the amount of arsenious oxide is more than 2.20 times that of the copper oxide, and the natural inference is that either arsenic has been added purposely or that the material has been carelessly manufactured.

A comparison of the water-soluble arsenic in Paris green and lead acetate emphasizes one of the chief advantages gained by using the latter insecticide. In lead arsenate from 0.22 to 1.31 per cent. was soluble in ten days, while in Paris green the solubility ranged from 2.44 to 10.72 per cent.

II. DIRECTIONS FOR THE USE OF LEAD ARSENATE AND PARIS GREEN AS INSECTICIDES.

By W. E. BRITTON, *Entomologist*.

Lead arsenate as an insecticide was first used in the work of the Gypsy Moth Commission in Massachusetts in the early nineties and it has since been employed in controlling nearly all of the leaf-eating insects, and has proved to be a valuable addition to our list of available arsenical poisons. When devoured by insects it is somewhat slower in its action than Paris green, and should therefore be applied earlier, before much damage has been done to the plants. On account of the excellent adhesive qualities of lead arsenate, it remains upon the foliage for a long time, while Paris green soon washes off if rains are frequent. Lead arsenate is gradually replacing Paris green as an arsenical insecticide, and especially during the past season the high price of the latter has induced many farmers and fruit growers to use lead arsenate. Paris green has been used to destroy leaf-eating insects ever since the Colorado potato beetle reached the Atlantic States. It is therefore the old standard remedy, and in many places is the only arsenical insecticide that can be purchased at the stores.

FORMULA FOR LEAD ARSENATE.

As lead arsenate is sold in paste form, and even when calculated as water-free contains less arsenic than Paris green, it is necessary to use a larger quantity by weight of the commercial article to gain the desired end in spraying work. Lead arsenate can be used only in liquid form to be sprayed upon the foliage, and the usual formula is as follows:

Lead arsenate.....	3 lbs.
Water	50 gallons.

For sawfly larvae and some other insects that are easy to kill, one pound in fifty gallons may suffice, and in spraying to kill gypsy caterpillars five pounds in fifty gallons are the proportions considered the most effective. In spraying for elm leaf beetle larvae the poison should be directed against the under sides of

the leaves. The amount of lead arsenate may be increased greatly without danger of injuring the foliage, and lime should not be added. Lead arsenate can be used in connection with Bordeaux mixture, though it is thought to be slightly less effective as an insecticide when used in this way.*

FORMULA FOR PARIS GREEN.

Paris green is put up in powder form and can be applied either dry or as a liquid. On account of the soluble acid which it contains (see page 9 of this bulletin) there is always danger of "burning" the foliage unless some alkali is used with the poison. For this purpose lime is usually recommended, and the adhesiveness of the mixture is greatly improved by the lime. About three pounds of lime should be used for each pound of Paris green. If to be applied dry in a duster or powder gun, Paris green should be mixed thoroughly with air-slaked lime or land plaster in the following proportions:

Paris green	1 pound.
Air-slaked lime	100 pounds.

For use as a spray Paris green may be prepared as follows:

Paris green.....	1 pound.
Fresh quicklime	3 pounds.
Water	100 gallons.

In most orchards and potato fields Paris green is used in connection with Bordeaux mixture, and as this contains an excess of lime, no more lime is added.

* Tests made at this Station show that the presence of the Bordeaux mixture renders the lead arsenate perfectly insoluble. This perhaps may account for its lessened poisonous effect on insects.



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